Hydrogenation of COED Coal Oils

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Introduction

The Office of Coal Research, Department of the Interior, has sponsored several projects having as one of their objectives, the production of oil from coal. One of these, project COED, conducted by FMC Corporation, produces oil by low temperature pyrolysis of coal. The Atlantic Richfield Company, which had been conducting hydrogenation experiments on coal derived oils, was requested by the Office of Coal Research to hydrotreat some COED oils. Accordingly, the following work was carried out by ARCO in cooperation with FMC.

Raw oils from the COED process have a low hydrogen content and high concentrations of oxygen, nitrogen, and sulfur. Hence, hydrotreating is required before the oils can be used in present day petroleum refining processes. In the COED process, the oil product is taken from the reactors as a vapor, leaving the residual ash and char to be withdrawn separately as a fluidized solid. Any entrained solids in the oil vapor are removed by cyclones and by filters. Consequently the COED oil, being virtually solids free, can be hydrotreated in fixed bed reactors.

Hydrogenation Equipment

The equipment used by the ARCO laboratories is a typical bench scale high-temperature, high-pressure continuous unit of the type used in petroleum process research. The unit is shown schematically in Figure 1. The oil in a heated, gas blanketed charge tank is circulated by a low pressure, positive displacement pump. This serves to maintain a uniform mixture in the feed tank and to supply a positive pressure at the suction of the high pressure feed pump. The oil is combined with hydrogen and preheated before passing downflow through the 14 inch catalyst bed. The product is cooled and separated into gas and liquid fractions for sampling and analysis.

The double pumping system reduced the problem of interruption of flow. COED oil, being a pyrolysis product, can form polymers and coke at temperatures above 600°F. This is not a problem as long as liquid flow is maintained. However, if the flow is interrupted, the oil does not drain from the reactor fast enough to avoid coking.

The catalyst used is commercially available HDS-3A manufactured by American Cyanamid. It is a 1/16-inch extrudate containing 3% NiO and 15% MoO$_3$ on alumina.

Results of Hydrogenation

COED oils from three coals were charged. Their composition and gravity are shown in Table I.

Table I

PROPERTIES OF HYDROGENATION FEEDS

Oil Source	% C	% H	% O	% N	% S	Density, °API
Utah	83.3	8.5	6.8	1.1	.34	-3.5°
Illinois No. 6	80.1	7.2	9.1	1.1	2.50	-13.1°
Pittsburgh Seam	83.3	7.1	6.6	1.2	1.80	-12.3°

The Utah and Illinois No. 6 are high-volatile B bituminous coals. Pittsburgh seam is a high volatile A bituminous coal. The major differences between the oils are the lighter density, lower sulfur, and higher hydrogen content of the Utah oil. The Illinois No. 6 oil is highest in sulfur and oxygen.

All of the hydrogenation experiments discussed in this report, were conducted at 3000 psig. Hydrogen flow rates were generally between 8,000 and 12,000 SCF/Bbl. Variations in hydrogen rates did not have a significant effect on the hydrogenation reactions. The process variables were space velocity and temperature. The latter ranged from 650° to 850°F. and space velocities (WHSV) of 0.3 to 3.0 lbs./hr. of oil per lb. of catalyst were used.

Hydrogen consumption was between 1500 to 4500 SCF/Bbl. The exothermic reaction resulted in an uneven temperature profile in the catalyst bed. In a typical run the temperature rose 65° in the first 2 to 4 inches of the bed. The temperature then declined gradually in the remaining bed as the heat sink of the reactor and furnace removed heat from the system. The temperatures used for correlating the data are arithmetic averages of temperatures taken at one-inch intervals in the bed. This average temperature is about 20° less than the maximum temperature.

The data on removal of oxygen, nitrogen and sulfur were correlated by simple first-order kinetics. Figure 2 shows the removal of nitrogen from Illinois No. 6 oil. Nitrogen removal is plotted as a function of reciprocal space velocity and temperature. The temperature factor indicates an activation energy of 29,000 BTU per lb. mol. The temperature factor was obtained by first plotting the nitrogen removal vs. reciprocal space velocity. Deviations from a line through the data were plotted against temperature.

Figures 3 and 4 show similar correlation for oxygen removal and sulfur removal from Illinois No. 6 oil. Indicated activation energies are 15,000 BTU per lb. mol. for oxygen and 9,500 BTU per lb. mol. for sulfur removal. Qadar, Wiser and Hill[1] found that the activation energies for nitrogen and sulfur removal from a low temperature coal tar changed at about 750°F. The general scatter of the data and the method of determining average temperature in this work preclude the identification of different activation energies above and below 750°F.

Nitrogen is the most difficult of the heteroatoms to be removed. At 720°F. and 1 WHSV the removals from Illinois No. 6 oil are as follows: Nitrogen, 72%; Oxygen, 91%; and Sulfur, 98%.

The examination of the heteroatom removal from the other oils disclosed that the temperature trends found for the Illinois No. 6 oil also applied to all three. However, the reaction rates vary with the oils. Figure 5 shows that for nitrogen removal, the Utah oil requires only two-thirds the severity of the Illinois No. 6 oil. The Pittsburgh oil requires twice the severity of the Illinois No. 6 oil. Figure 6 shows oxygen removal. Pittsburgh oil requires 2½ times the severity of Illinois No. 6, and Utah oil needs 80% of the Illinois No. 6 severity. Sulfur removal shown in Figure 7 is slightly different. Pittsburgh oil needs 2.3 times the Illinois severity. Sulfur removal from Utah oil is indicated to be more difficult than from Illinois No. 6 oil. This difference may not be real. Because of

the low 0.3% sulfur content of the Utah oil feed, there is more scatter in the data on this feed than the other two.

The required space velocities for 80% oxygen, nitrogen and sulfur removal from the three oils are given in Table II.

Table II

SPACE VELOCITIES FOR 80% REMOVAL
CONDITIONS, 720°F. AND 3000 PSIG.

	80% Nitrogen Removal WHSV	80% Oxygen Removal WHSV	80% Sulfur Removal WHSV
Utah	1.2	1.8	1.8
Illinois No. 6	.8	1.5	2.6
Pittsburgh	.4	.6	1.1

Total hydrogen consumption was also correlated by pseudo first order kinetics. First the quantity of hydrogen required to convert the oil to cycloparaffins (C_nH_{2n}) and to remove all oxygen, nitrogen and sulfur as water, ammonia, and hydrogen sulfide was determined. This hydrogen saturation value assumes no cracking.

Oil Source	Hydrogen for Total Saturation
Utah	4600 SCF/Bbl.
Illinois No. 6	6200 SCF/Bbl.
Pittsburgh	6400 SCF/Bbl.

The observed hydrogen consumption, divided by the quantity needed for total saturation is reported as the percent hydrogen saturation. This value was then plotted as a function of reciprocal space velocity and temperature in the same manner as for heteroatom removal. As seen on Figure 8, when plotted in this manner, the data from Utah and Illinois No. 6 oils fall on a common line. The Pittsburgh oil requires $2\frac{1}{2}$ times as much severity to obtain a similar degree of saturation.

This method of correlating hydrogen consumption ignores any effect the approach to equilibrium may have on the rate of hydrogen usage. The fact that the data plots as well as it does indicates that the reactions are not equilibrium controlled.

The reasons for the differences in ease of hydrogenation and heteroatom removal for the three oils are not known, but they are probably related to the hydrogen-carbon ratio of the oils. The atomic ratios of the oils are as follows:

	H/C Ratio
Utah	1.22/1
Illinois No. 6	1.08/1
Pittsburgh	1.02/1

The last reaction examined is the production of gas by cracking. As seen in Figure 9, the gas yield climbs precipitously at temperatures above 780°F. The effect of temperature is so overwhelming that no trends with space velocity could be obtained. Cracking of all three oils fall on a common temperature line. This data indicates the necessity of keeping the catalyst bed temperature below 780°F. if oil is the desired product.

No catalyst life studies were made, but it is anticipated that catalyst life would be related inversely to the gas production.

Properties of the Hydrogenated Oils

The °API gravity of the products varies directly with the hydrogen consumption. However, as shown in Figure 10 the oils fall on three separate lines. For example, the production of a 25°API hydrogenated oil from Utah oil needs only 2700 SCF/Bbl. A similar product from Illinois No. 6 oil would need 4050 SCF/Bbl. and the Pittsburgh Seam oil would use 4550 SCF/Bbl.

Distillation curves of the three oil feeds and three products that were made with similar hydrogen consumption are shown in Figure 11. The consumption of 3600 SCF of hydrogen per barrel lowers the boiling range of each oil about 300°F. It should be noted that there is little, if any, residuum (material boiling above 1000°F.) left in these oils.

The properties of these three product oils are as follows:

Table III

PROPERTIES OF HYDROGENATED OIL PRODUCT

Oil Source	Utah	Illinois No. 6	Pittsburgh
Conditions			
Weight hourly space velocity	0.75	1.3	0.50
Temperature, °F.	748°	798°	742°
Pressure, PSIG	3000	3000	3000
Hydrogen Consumption, SCF/Bbl	3500	3600	3700
C_4+ Liquid Product			
°API	31.8°	22.5°	19.6°
Viscosity, SUS @ 180°F.	34.6	----	44.9
Pour Point, °F.	80°	30°	20°
Ramsbottom Carbon, Wt. %	0.44	----	3.85
% H	12.7	----	10.9
% O	0.13	----	0.7
% N	0.05	----	0.14
% S	< 50 ppm	----	0.03

The high pour point of the Utah oil product is caused by a larger paraffin content. A comparison of the reformer stock and middle distillate fractions from Utah and Pittsburgh oils shows this difference.

Table IV

PROPERTIES OF PRODUCT FRACTIONS

Oil Source	Utah	Pittsburgh
Reformer Stock (C_6-400°F.)		
Yield, Vol. %	12.5	9.6
°API	38.7°	37.6°
Paraffins, Vol. %	18	6
Cycloparaffins, Vol. %	65	74
Aromatics, Vol. %	17	20

Oxygen, Wt. %	.06	.47
Nitrogen, Wt. %	.10	.09
Sulfur	Trace	5 ppm

Middle Distillate (400-650°F.)

Yield, Vol. %	68.2	38.9
°API	30.1°	22.5°
Paraffins, Vol. %	25	1
Cycloparaffins, Vol. %	39	55
Aromatics, Vol. %	36	44
Oxygen, Wt. %	.20	.48
Nitrogen, Wt. %	.06	.12
Sulfur	Trace	30 ppm

The two reformer stocks above are satisfactory reformer feeds after conventional pretreat steps to remove the residual oxygen and nitrogen. The high concentration of ring structures indicates that only a very mild reforming severity is needed to produce a high octane naphtha. The middle distillates can be used as heating oils, or after oxygen and nitrogen removal, by conventional pretreating, they can be charged to a hydrocracker for additional gasoline production.

The high cycloparaffin content of the hydrogenated COED oils would classify the syncrudes as the naphthenic type. Although the °API gravity of these oils may be lower than most crude oils, they contain much less residuum than typical crudes. These hydrogenated COED coal oil syncrudes can be processed in typical petroleum refinery units.

Conclusion

In summary, the removal of heteroatoms and the gross hydrogen consumption occurring during the hydrogenation of COED coal oils can be correlated by simple, first-order kinetics. The oil from Pittsburgh seam coal is more difficult to hydrogenate than the oils from Utah and Illinois No. 6 coals. The Utah oil requires less hydrogen consumption than the other two to produce a superior oil.
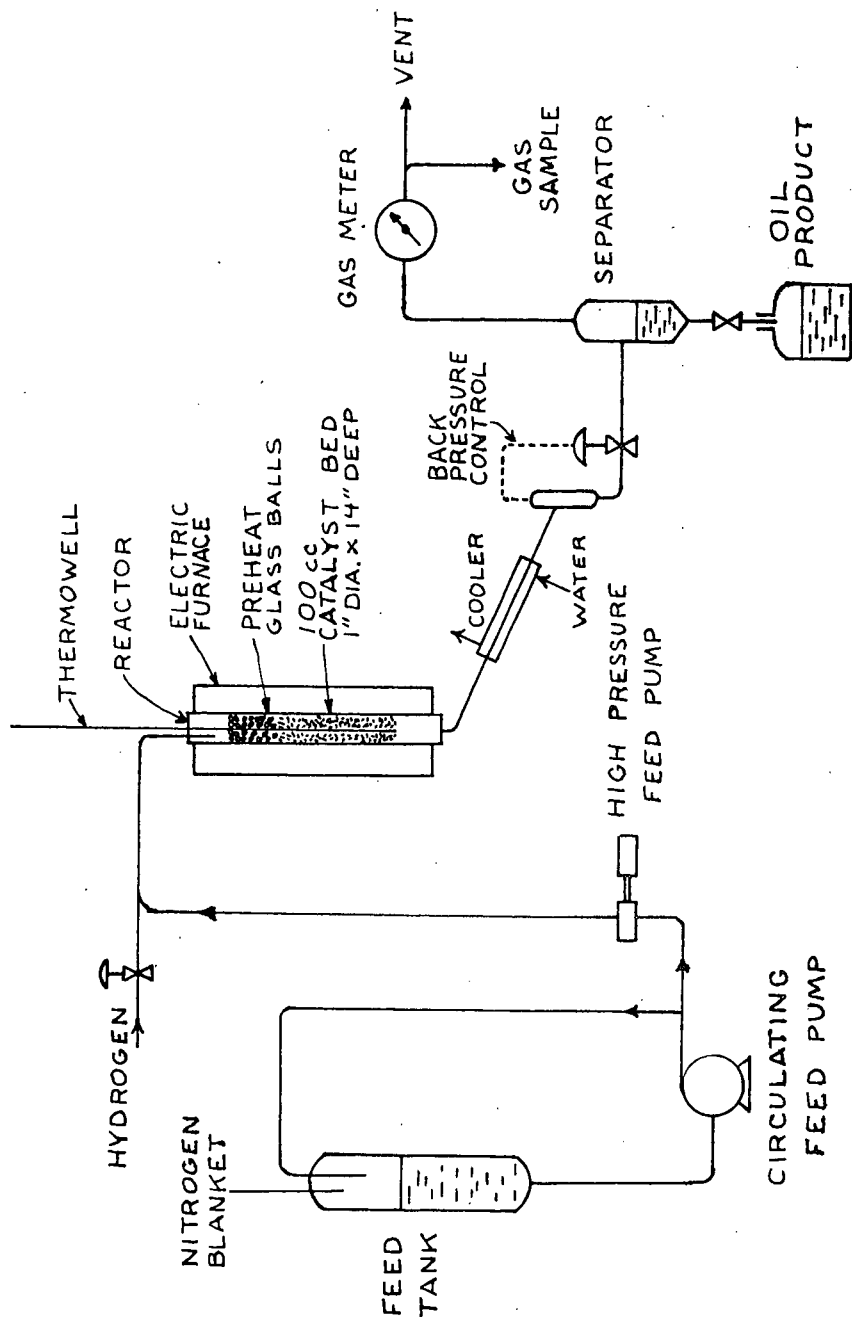
The product oils are naphthenic, containing high cycloparaffin concentrations. They contain little residuum and can be processed by conventional petroleum refining methods.

Bibliography

1. Qadar, Wiser and Hill, I and EC Process Design and Development, 7, No. 5, 390-397, July 1968.

FIG. 1

HYDROGENATION UNIT

HYDROGENATION OF COED ILLINOIS NO.6 COAL OIL
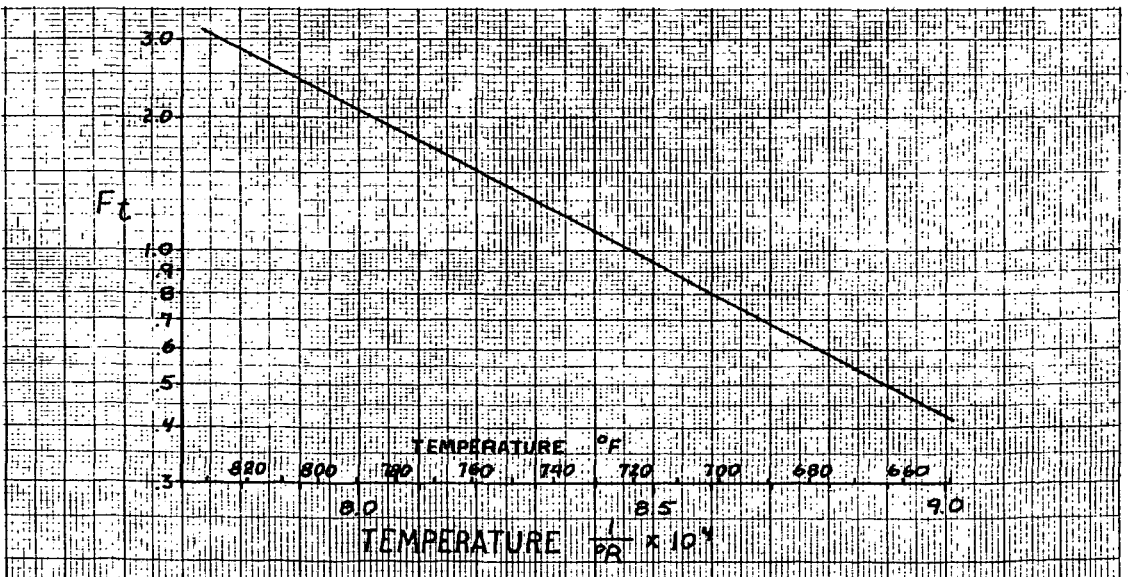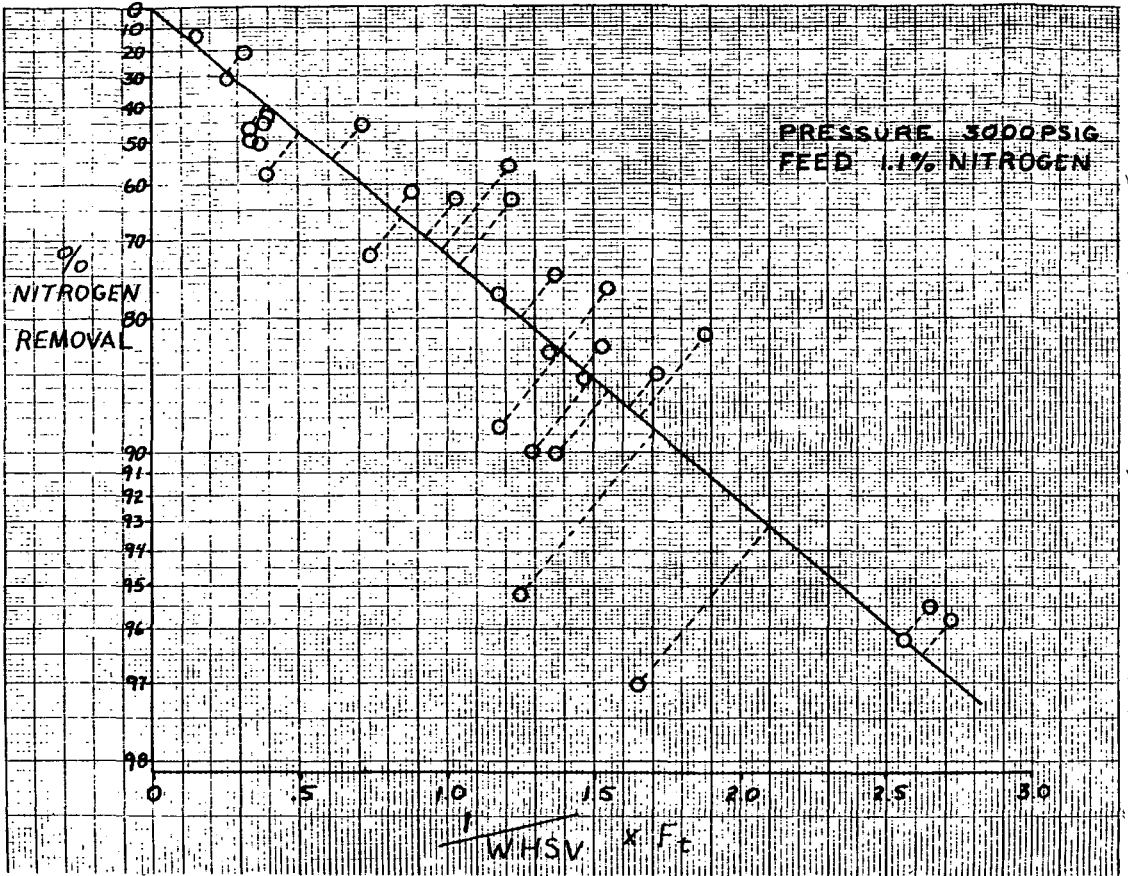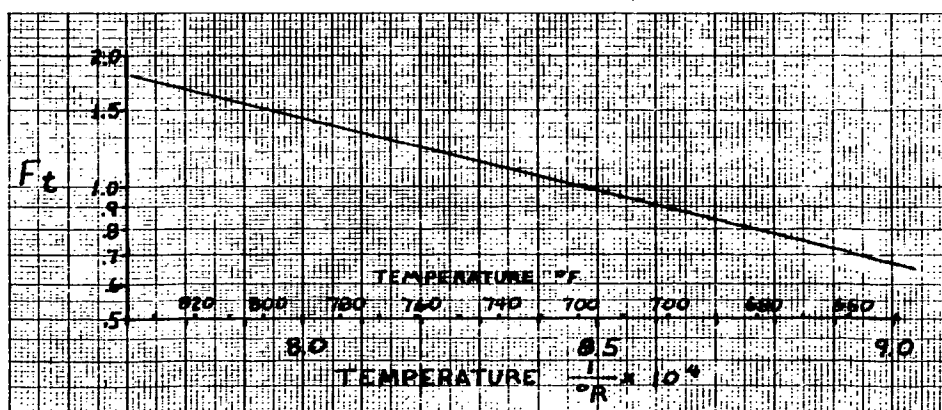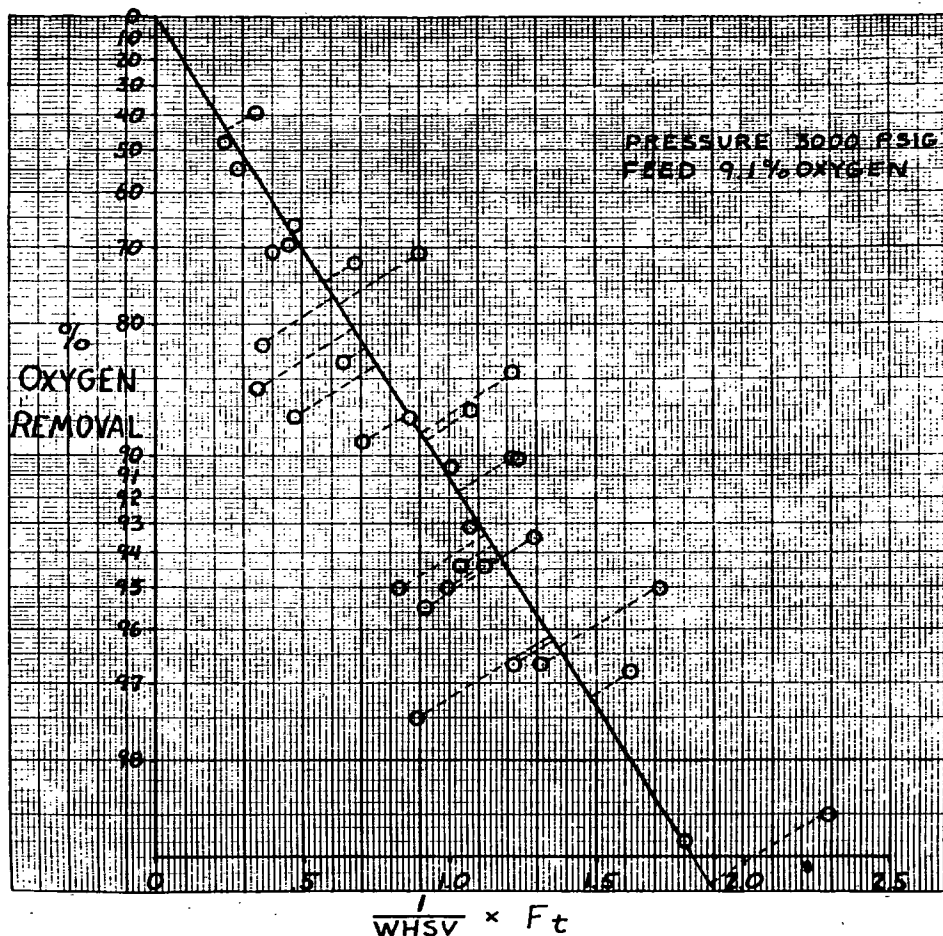
NITROGEN REMOVAL

FIG. 2

HYDROGENATION OF COED ILLINOIS NO. 6 COAL OIL

FIG. 3

OXYGEN REMOVAL

$$\frac{1}{WHSV} \times F_t$$

PRESSURE 3000 PSIG
FEED 9.1% OXYGEN

% OXYGEN REMOVAL

F_t

TEMPERATURE °F

$$TEMPERATURE \quad \frac{1}{°R} \times 10^4$$

HYDROGENATION OF COED ILLINOIS NO·6 COAL OIL

SULFUR REMOVAL

FIG. 4
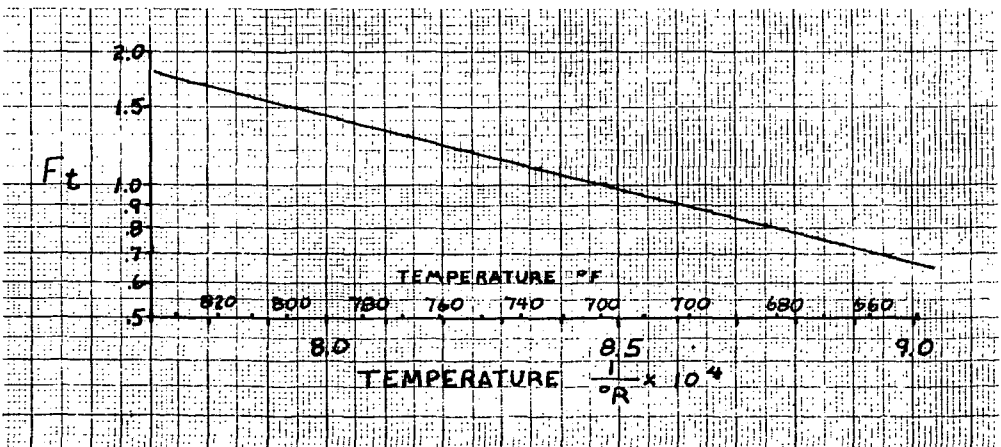

PRESSURE 3000 PSIG
FEED 2.5% SULFUR
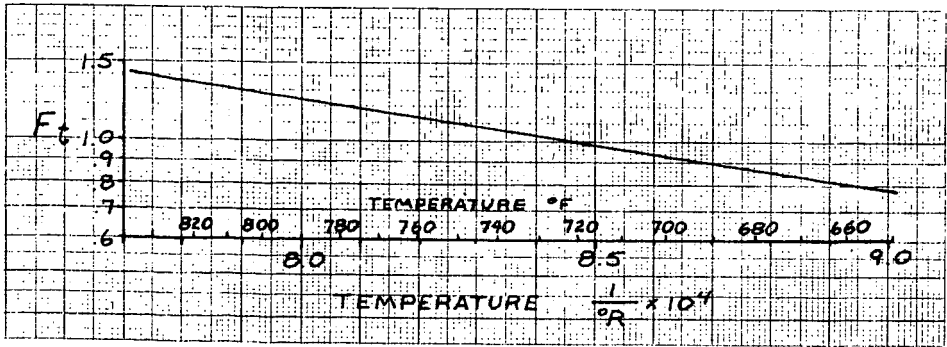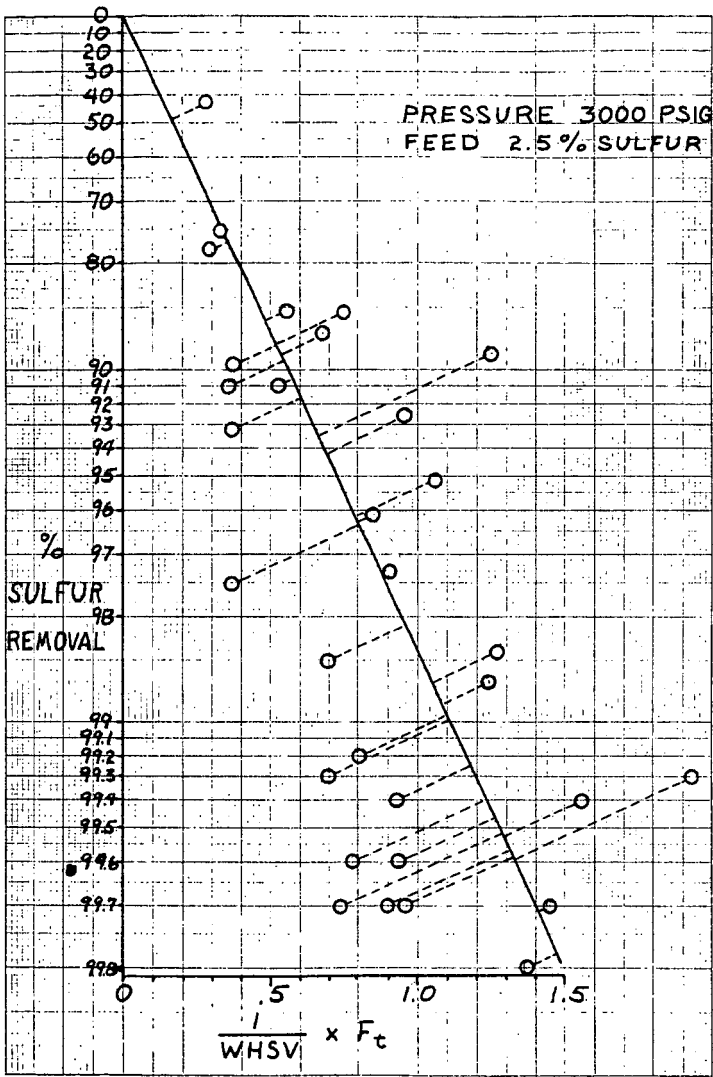
HYDROGENATION OF COED COAL OILS
NITROGEN REMOVAL
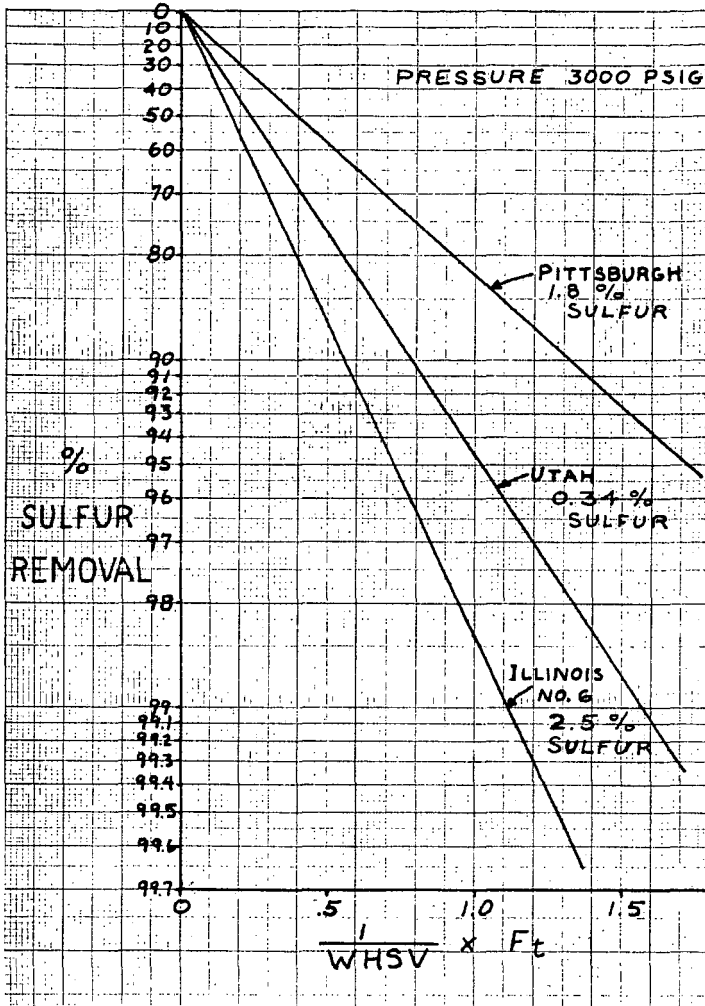### FIG. 5
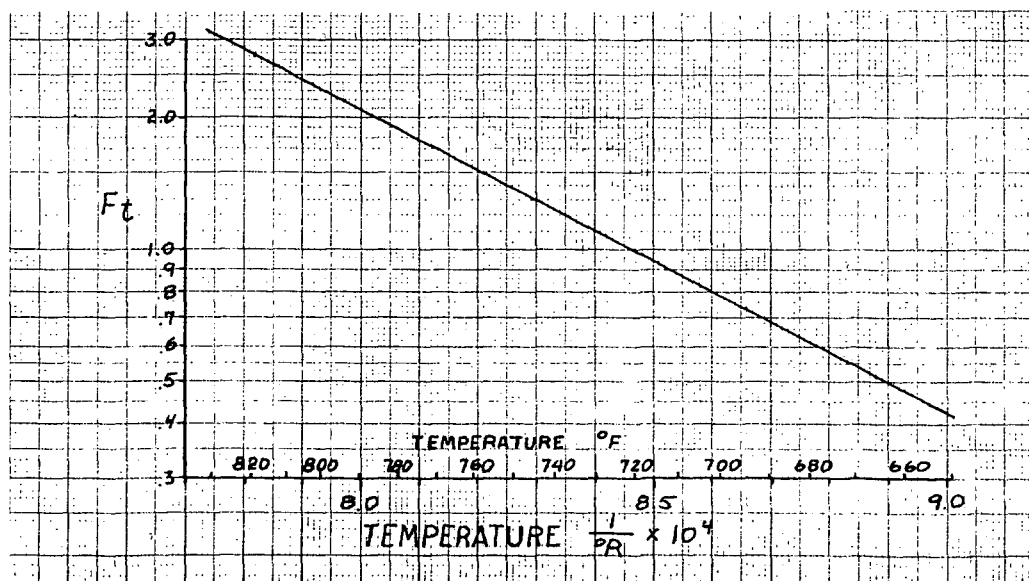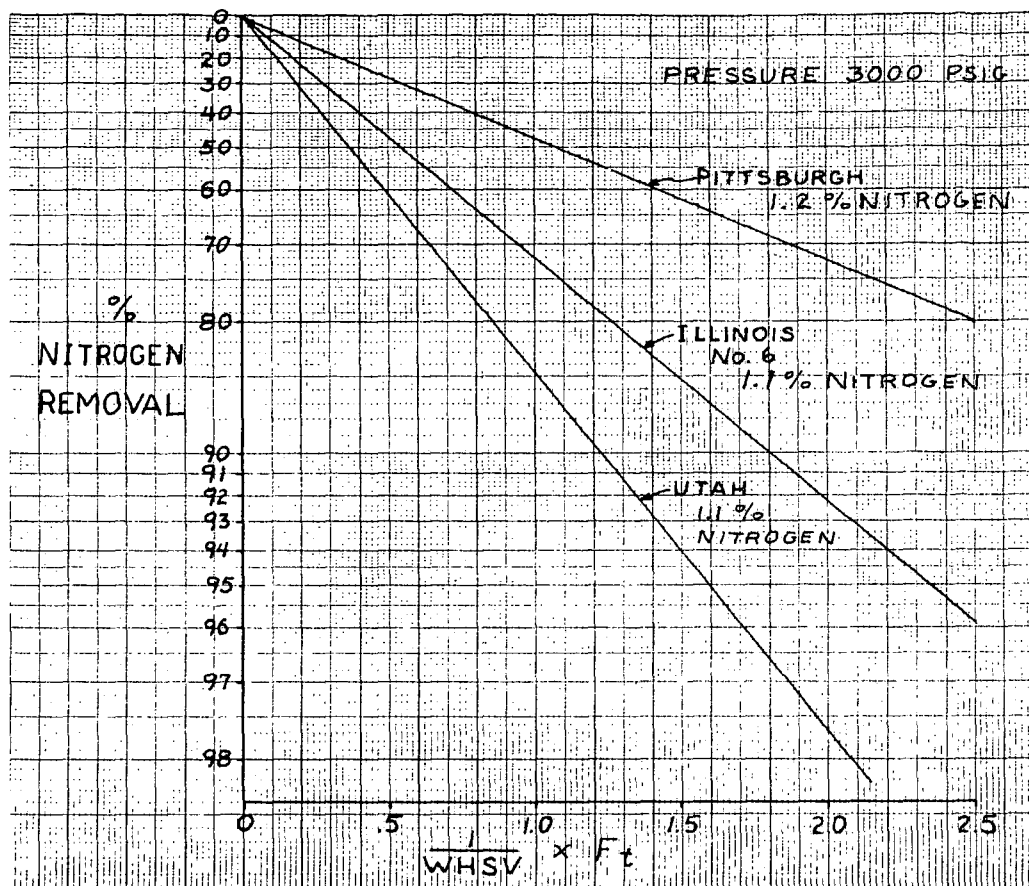
HYDROGENATION OF COED COAL OILS

OXYGEN REMOVAL

FIG. 6
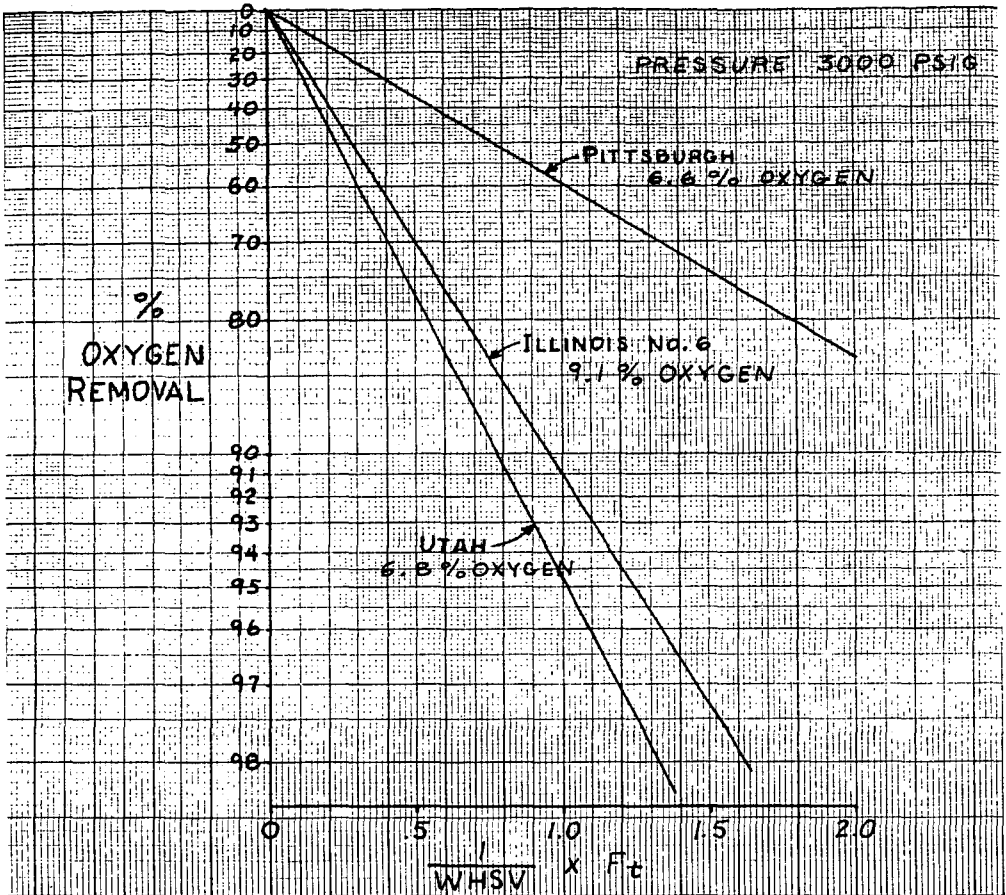
HYDROGENATION OF COED COAL OILS

SULFUR REMOVAL

FIG. 7

Upper chart axes: vertical axis labeled **% SULFUR REMOVAL** (scale from 0 at top to 99.7 at bottom); horizontal axis labeled $\frac{1}{WHSV} \times F_t$ (scale 0, .5, 1.0, 1.5). Annotation: PRESSURE 3000 PSIG. Curves labeled PITTSBURGH 1.8 % SULFUR; UTAH 0.34 % SULFUR; ILLINOIS NO. 6 2.5 % SULFUR.

Lower chart axes: vertical axis labeled F_t (scale 1.5, 1.0, .9, .8, .7, .6); horizontal axis labeled TEMPERATURE °F (820, 800, 780, 760, 740, 720, 700, 680, 660) and TEMPERATURE $\frac{1}{°R} \times 10^4$ (8.0, 8.5, 9.0).

HYDROGENATION OF COED COAL OILS
PERCENT HYDROGEN SATURATION   FIG. 8

FIG. 9

HYDROGENATION OF COED COAL OILS
GAS YIELDS

SYMBOL	OIL SOURCE
△	UTAH
○	ILLINOIS NO. 6
□	PITTSBURGH

WT. %
C₃'s and
LIGHTER
GAS YIELD

TEMPERATURE °F
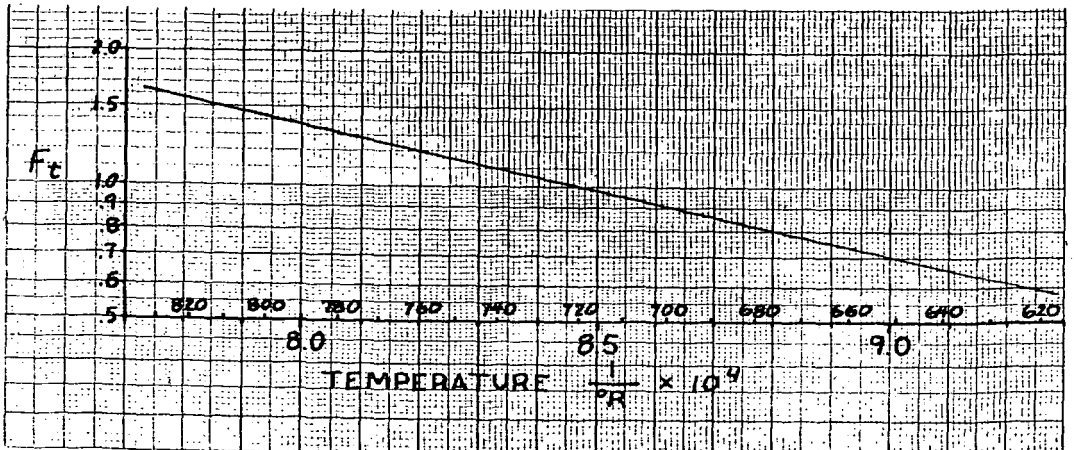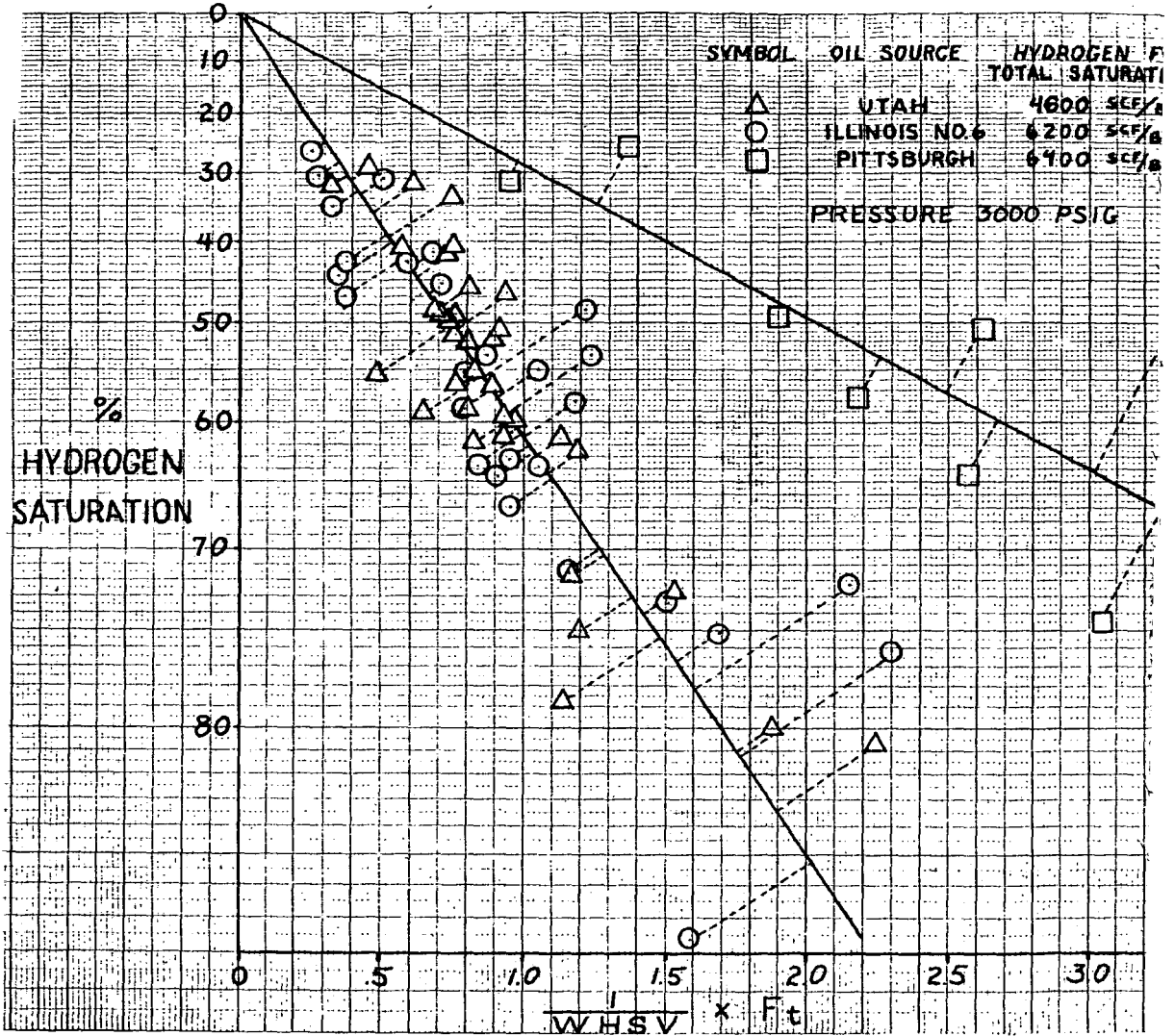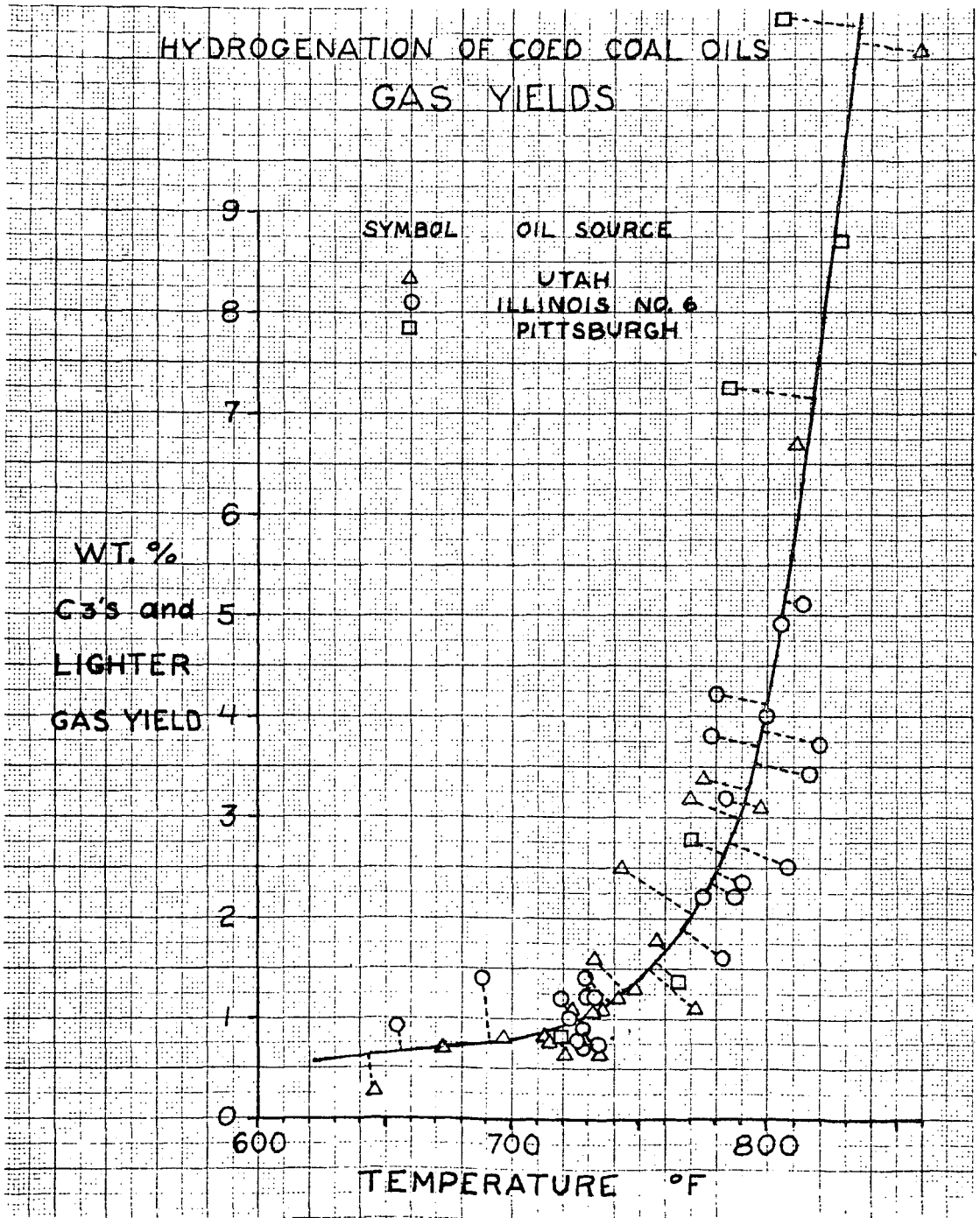
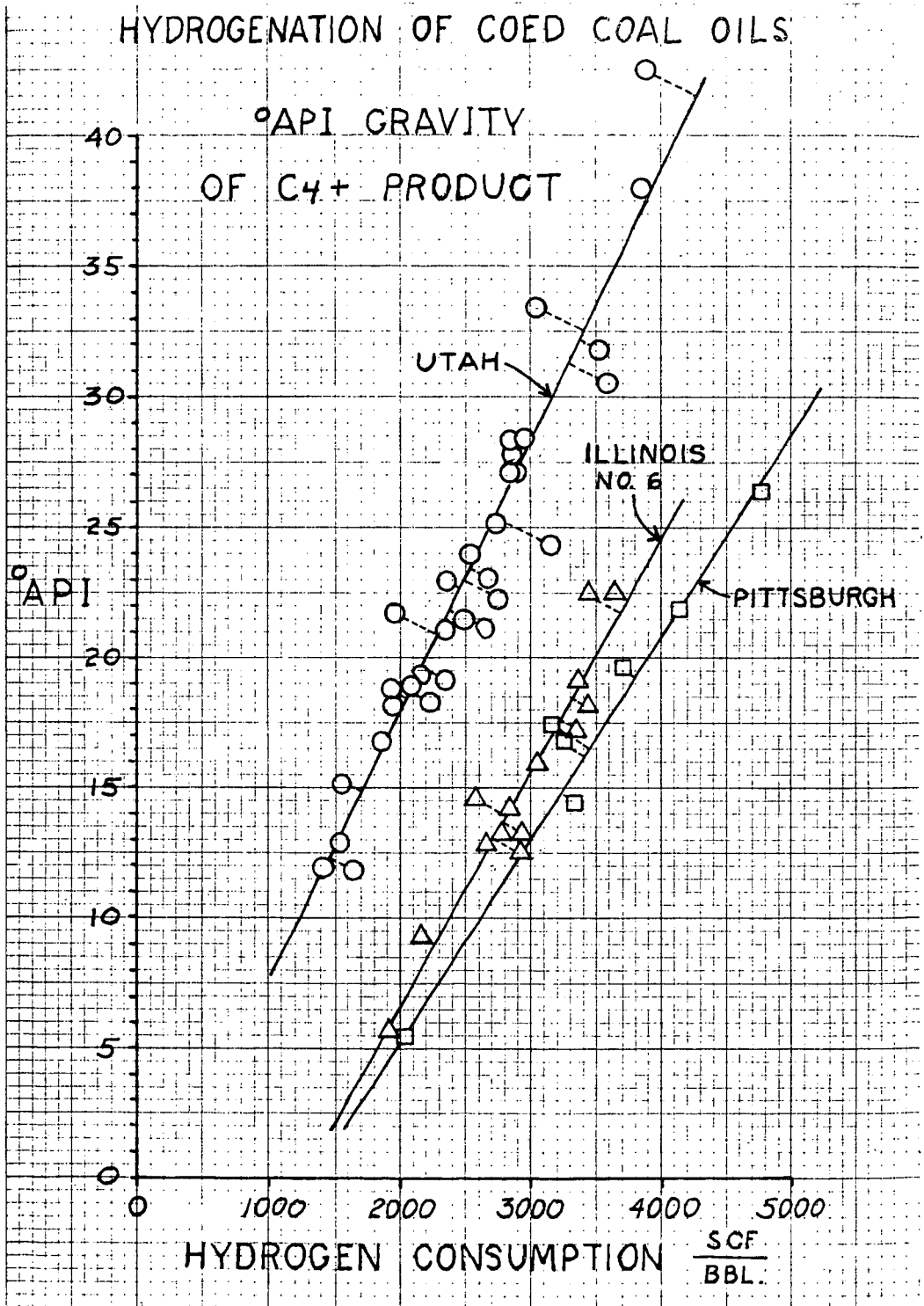FIG. 10

HYDROGENATION OF COED COAL OILS

FIG. 11

HYDROGENATION OF COED COAL OILS
DISTILLATION OF FEED AND PRODUCTS